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Tetraphenylhexaazaanthracene: A Case for Dominance of Cyanine Ion Stabilization Overwhelming 16π Antiaromaticity

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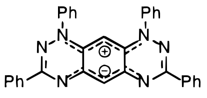
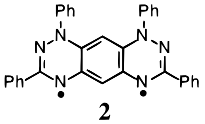
While the tetraphenylhexaazaanthracene's (TPHA, **1**) skeleton was reported in 1908,[1] neither the parent nor its derivatives have appeared in the literature. TPHA was prepared in our laboratories following Scheme 1.



1 TPHA



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The major product was atmosphere-stable, highly fluorescent, thermally stable up to 400 °C, and exhibited sharp-line NMR spectra (^{1}H and ^{13}C) yet was ESR silent, demanding a closed shell species with skeleton **1** and not **2** (see structures above and Figures 1 and 2).[2b] X-ray crystallography confirmed the zwitterionic structure **1**, further verified by theoretical calculations on a model, **6**.[2−6]

X-ray diffraction analysis of **1** revealed a monoclinic unit cell,[7] where zwitterionic molecules are arranged in stacks along the shortest crystallographic *c* axis. The negative and positive charges are delocalized along N(1)C(3)C$^-$(5)C(7)N(6) and N(3)C(2)C$^+$(4)C(6)N(4), respectively (Figure 2). Similar bond lengths have been previously found in some cyanine dyes[8,9] and zwitterionic structures.[10,11] Taking into account that CN bonds are, on the average, 0.1 Å shorter than CC bonds, the N(1)C(3)C(5)C(7)N(6) and N(3)C(2)C(4)C(6)N(4) arrays show a remarkable bond equalization, particularly in the central hexagon [C(2)−C(4)−C(6) and C(3)−C(5)−C(7)].

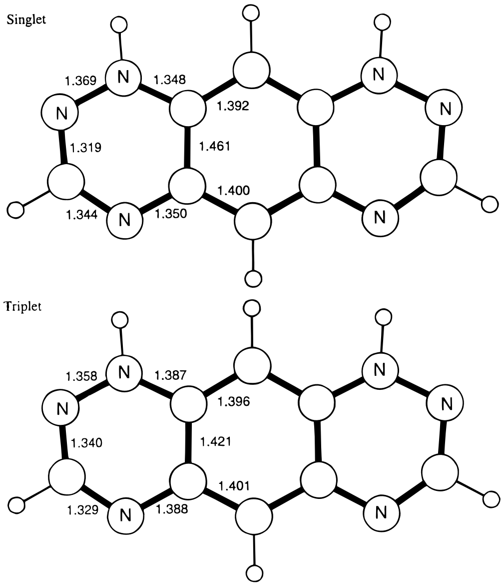


Figure 1. Singlet and triplet structure of the model compound **6** optimized with the (U)B3LYP/6-31G* method.

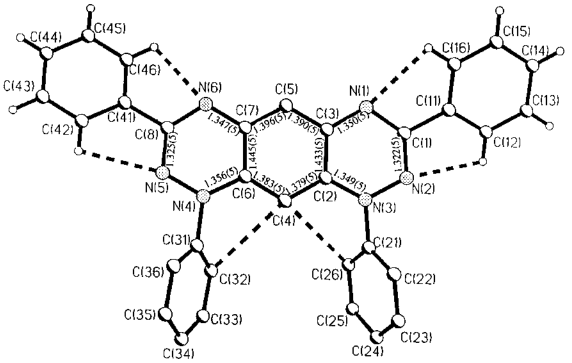
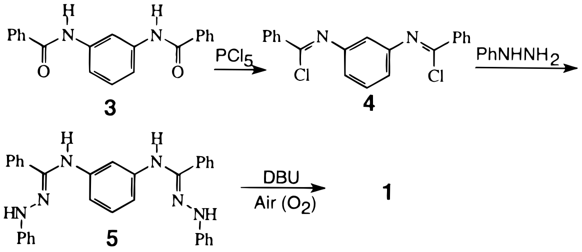


Figure 2. Molecular structure for TPHA with atomic labeling. Dotted lines represent short intramolecular contacts.

Scheme 1. Synthetic Route to TPHA.



The calculated charge distribution agrees with a zwitterionic ground-state structure. The Mulliken charges are +0.33 for the positively charged part N(3)C(2)C(4)C(6)N(4) of the zwitterion and −0.33 for the remainder. The calculated dipole moment is 5.1 D. For comparison, the same type of calculation for the simple zwitterion, $^-CH_2NH_3^+$, shows a charge separation of 0.33 e.

The geometries of isolated charged fragments, **7** and **8**, are compared in Figure 3. The differences in the calculated bond lengths between these fragments and the zwitterion **6** can be attributed to the electrostatic interactions across four single bond junctions uniting these fragments. The charge distributions of the isolated fragments are comparable to that of the zwitterion. In the positively charged cyanine, **7**, the outer carbons bear the positive charge, as in the zwitterion itself. In fragment **8**, the negative part of the zwitterion, most of the negative charge resides at the two terminal amidine nitrogens.

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[1] Pierron, P. *Ann. Chim. Phys.* **1908**, *15*, 269.

[2] (a) Geometry optimizations were performed with density functional theory (DFT)[3] using the program Gaussian 94.[4] The B3LYP functional[5] and split valence 6-31G* basis set were employed.[6] Phenyl substituents were replaced by hydrogen in the model system. The optimized singlet and triplet structures of the zwitterion are shown in Figure 1. (b) However, phenylaminyl radicals were calculated to be π-type: Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int Ed. Engl.* **1975**, 14, 783.

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[4] Frisch, M. J. et al. *Gaussian 94, Revision B.2*; Gaussian, Inc.: Pittsburgh, PA, 1995.

[5] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372, 5648.

[6] B3LYP/6-31G* calculations predict a singlet−triplet gap of 39 kcal/mol for anthracene (experiment = 42 kcal/mol).

[7] Crystal data for $C_{32}H_{22}N_6$: FW = 490.56, monoclinic, $P2_1/c$, with dimensions $a = 13.492(14)$ Å, $b = 21.817(2)$ Å, $c = 8.5884(9)$ Å, $\beta = 99.547(2)°$, $Z = 4$, $V = 2493.0(4)$ Å^3, $d_{\text{calcd}} = 1.307$ g cm^{-3}, $R(F) = 5.92\%$, $R_w(F^2) = 11.11\%$, μ(Mo Kα) = 0.080 mm^{-1}. $R(F) = \sum||F_o| - |F_c||/|F_o|$ with $F_o > 2.0\ \sigma(F)$. $R_w(F^2) = \sum(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 2.0\ \sigma(F)$. $w = 1/[\sigma^2(F_o^2) + (0.0612P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

[8] Declerq, J.-P.; Dubourg, A.; Payrastre, C.; Mazieres, M.-R.; Madaule, Y.; Wolf, J.-G. *Acta Crystallogr.* **1996**, *B52*, 500−504.

[9] Honda, M.; Katayama, C.; Tanaka, J. *Acta Crystallogr.* **1986**, *B42*, 90−95.

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[11] Heinemann, F.; Hartung, H. *Acta Crystallogr.* **1995**, *C51*, 442−445.

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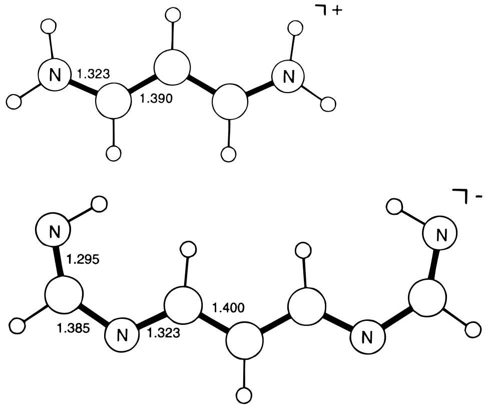

Figure 3. Isolated charged fragments **7** and **8** optimized by the (U)B3LYP/6-31G* method.

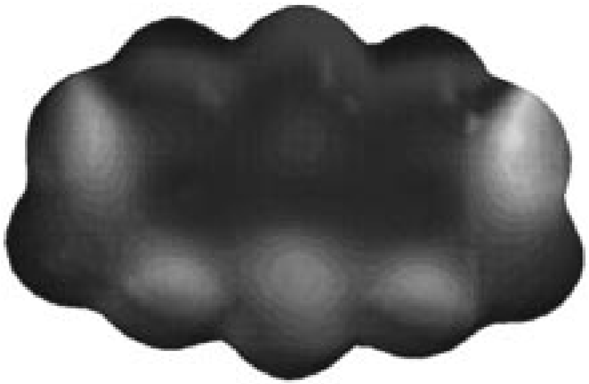

Figure 4. Electrostatic potential surface of **6**. Red represents a negative electrostatic potential, and blue represents a positive electrostatic potential.

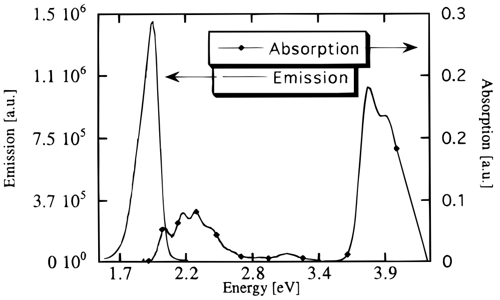

Figure 5. Emission and absorption spectrum of TPHA in toluene.

These results indicate that molecule **2**, by converting to **1**, *sacrifices the central benzene in favor of two independent cyanine subunits with a total of 16π electrons.* The hexaazaanthracene moiety is planar. The "peri" phenyl rings are twisted out of plane by ca. 62° and 65°. The other two phenyl rings attached to C(1) and C(8) are twisted out of the heteroanthracene plane by ca. 22° and 18°, respectively. The packing of the zwitterionic molecules within the stacks reflects the electrostatic attraction of the delocalized positive and negative charges [(+) over (−) over (+) over (−)...] with no exceptional intermolecular or interstack contacts.

The zwitterionic structure of TPHA could be perceived as a "double-barrel cyanine" dye. The electrostatic potential, plotted on an electron isodensity surface in Figure 4, clearly shows the charge polarization of the system. Cationic cyanine dyes are common, but stable anionic cyanines are rare.[12] Furthermore, this is the first synthesis of a molecule with such a nitrogen-based anionic cyanine dye moiety.[12−14]

TPHA exhibits two reductions,[15] $E^1_{1/2} = -1.36$ V and $E^2_{1/2} = -1.62$ V vs SCE, and one irreversible oxidation, $E_{1/2} = +0.55$ V vs SCE. Only the first reduction is both chemically and electrochemically reversible. Thus, zwitterion **1** is stabilized: the triplet state of **6** is predicted to be only 18.9 kcal/mol higher in energy.[6,16]

Unlike other dyes, the fluorescence of TPHA is not a mirror image of the absorption spectrum (Figure 5).[17] Singlet excited states of the zwitterions were computed with ab initio or semiempirical CI[18] calculations. Such calculations give reliable results for anthracene[19] and other extended conjugated systems. Ab initio CIS and semiempirical calculations on the model systems indicate that the low-lying excited states are $\pi\pi^*$ excited states, and the long wavelength transition is predicted to form an excited state which is qualitatively like the lowest triplet state. The second intense transition involves considerable charge transfer from the central ring to the two outer heterocyclic rings. Assuming that the emission band is due to the 3.8 eV absorption, the Stoke's shift is 15 000 cm^{-1} in toluene, which is roughly 3−25 times the typical Stoke's shift of other laser dyes.[20] The relative quantum yield[21] is 0.31 ± 0.03 in DMSO using rhodamine 640 as a reference.[22] There is no gain in emission intensity by degassing the solution with argon. The emission intensity is sensitive to concentration quenching for concentrations $>10^{-5}$ M. Also, the excitation profile varies with concentration, likely due to aggregation of the TPHA in solution,[23] and only emulates the UV−vis spectrum at concentrations $<10^{-5}$ M. The λ_{em} decreased from 633 nm in toluene ($\epsilon = 2.4$) to 619 nm in DMSO ($\epsilon = 47$). The unusual[17] observed trend is indicative of a polar ground state and nonpolar excited state, in excellent agreement with the calculated structures.

In conclusion, the first fully characterized derivative of hexaazaanthracene is a ground-state singlet; the triplet state is predicted to be 18.9 kcal/mol above. The zwitterionic singlet was characterized by X-ray, ^{1}H NMR, ^{13}C NMR, FTIR, UV, and mass spectroscopy. The bond lengths of the C−C bonds between the delocalized charges are similar to values observed for other cyanine dyes. Theoretical calculations support the zwitterionic proposal. The emission is considerably Stokes shifted from the absorption. Further studies and derivatization of TPHA are currently being pursued.

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Supporting Information Available: Experimental and crystallographic details (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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